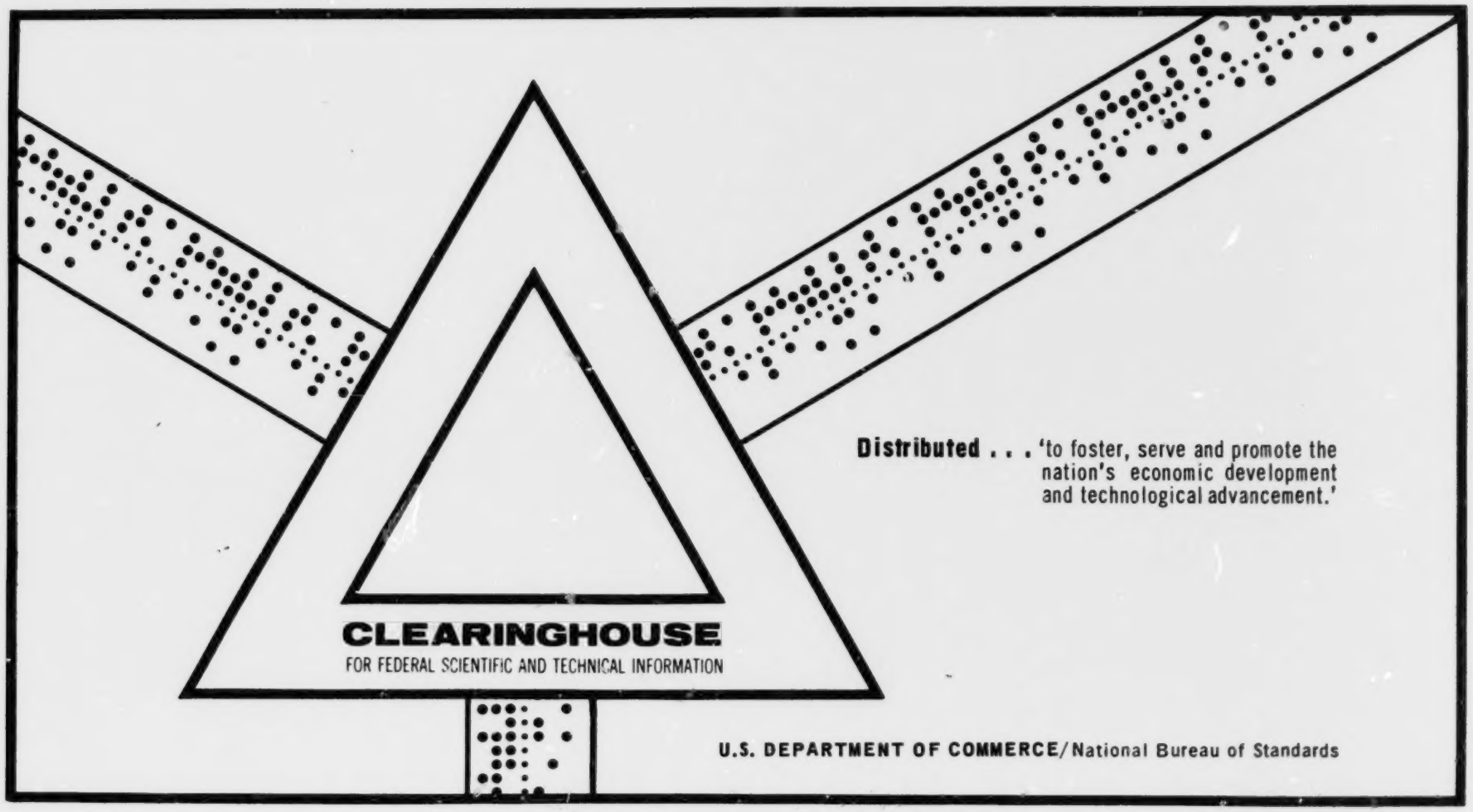
PB 188 070

AIR POLLUTION ASPECTS OF NICKEL AND ITS COMPOUNDS

Ralph J. Sullivan

Litton Systems, Incorporated
Bethesda, Maryland

September 1969


CLEARINGHOUSE
FOR FEDERAL SCIENTIFIC AND TECHNICAL INFORMATION
Distributed . . . 'to foster, serve and promote the nation's economic development and technological advancement.'
U.S. DEPARTMENT OF COMMERCE/National Bureau of Standards

This document has been approved for public release and sale.

PB188070

Reproduced by the
CLEARINGHOUSE
for Federal Scientific & Technical
Information Springfield Va. 22151

AIR POLLUTION ASPECTS

OF

NICKEL AND ITS COMPOUNDS

Prepared for the
National Air Pollution Control Administration
Consumer Protection & Environmental Health Service
Department of Health, Education, and Welfare
(Contract No. PH-22-68-25)

Compiled by Ralph J. Sullivan

Litton Systems, Inc.
Environmental Systems Division
7300 Pearl Street
Bethesda, Maryland 20014

September 1969

FOREWORD

As the concern for air quality grows, so does the concern over the less ubiquitous but potentially harmful contaminants that are in our atmosphere. Thirty such pollutants have been identified, and available information has been summarized in a series of reports describing their sources, distribution, effects, and control technology for their abatement.

A total of 27 reports have been prepared covering the 30 pollutants. These reports were developed under contract for the National Air Pollution Control Administration (NAPCA) by Litton Systems, Inc. The complete listing is as follows:

Aeroallergens (pollens)
Aldehydes (includes acrolein and formaldehyde)
Ammonia
Arsenic and Its Compounds
Asbestos
Barium and Its Compounds
Beryllium and Its Compounds
Biological Aerosols (microorganisms)
Boron and Its Compounds
Cadmium and Its Compounds
Chlorine Gas
Chromium and Its Compounds (includes chromic acid)
Ethylene
Hydrochloric Acid
Hydrogen Sulfide
Iron and Its Compounds
Manganese and Its Compounds
Mercury and Its Compounds
Nickel and Its Compounds
Odorous Compounds
Organic Carcinogens
Pesticides
Phosphorus and Its Compounds
Radioactive Substances
Selenium and Its Compounds
Vanadium and Its Compounds
Zinc and Its Compounds

These reports represent current state-of-the-art literature reviews supplemented by discussions with selected knowledgeable individuals both within and outside the Federal Government. They do not however presume to be a synthesis of available information but rather a summary without an attempt to interpret or reconcile conflicting data. The reports are

necessarily limited in their discussion of health effects for some pollutants to descriptions of occupational health exposures and animal laboratory studies since only a few epidemiologic studies were available.

Initially these reports were generally intended as internal documents within NAPCA to provide a basis for sound decision-making on program guidance for future research activities and to allow ranking of future activities relating to the development of criteria and control technology documents. However, it is apparent that these reports may also be of significant value to many others in air pollution control, such as State or local air pollution control officials, as a library of information on which to base informed decisions on pollutants to be controlled in their geographic areas. Additionally, these reports may stimulate scientific investigators to pursue research in needed areas. They also provide for the interested citizen readily available information about a given pollutant. Therefore, they are being given wide distribution with the assumption that they will be used with full knowledge of their value and limitations.

This series of reports was compiled and prepared by the Litton personnel listed below:

Ralph J. Sullivan
Quade R. Stahl, Ph.D.
Norman L. Durocher
Yanis C. Athanassiadis
Sydney Miner
Harold Finkelstein, Ph.D.
Douglas A. Olsen, Ph.D.
James L. Haynes

The NAPCA project officer for the contract was Ronald C. Campbell, assisted by Dr. Emanuel Landau and Gerald Chapman.

Appreciation is expressed to the many individuals both outside and within NAPCA who provided information and reviewed draft copies of these reports. Appreciation is also expressed to the NAPCA Office of Technical Information and Publications for their support in providing a significant portion of the technical literature.

ABSTRACT

Inhalation of nickel or its compounds may cause cancer of the lung, cancer of the sinus or other disorders of the respiratory system, or dermatitis. No information was found on the effects of nickel air pollution on commercial animals, plants, and materials. The most likely sources of nickel in urban air are emissions from metallurgical plants using nickel, engines burning fuels containing nickel additives, burning coal and oil, nickel plating facilities, and incineration of nickel products. In 1964, concentrations of nickel in urban air averaged 0.032 $\mu g/m^3$ and ranged up to a maximum of 0.690 $\mu g/m^3$.

Nickel as a particulate presents no special abatement problems and will be controlled with the total particulates. Gaseous nickel carbonyl will have to be thermally decomposed before it can be removed as particulate. No information has been found on the economic costs of nickel air pollution or on the costs of its abatement. Analytical methods are available to measure nickel at the 0.006 $\mu g/m^3$ level and nickel carbonyl at the 7 $\mu g/m^3$ level.

CONTENTS: Nickel's and nickel compounds

FOREWORD

ABSTRACT

1. INTRODUCTION 1

2. EFFECTS 2

2.1 Effects on Humans 2
2.1.1 Dermatitis 3
2.1.2 Respiratory Disorders 5
2.1.3 Cancer of the Respiratory Tract 6
2.2 Effects on Animals 12
2.2.1 Commercial and Domestic Animals 12
2.2.2 Experimental Animals 13
2.2.2.1 Toxicity 13
2.2.2.2 Carcinogenicity 15
2.3 Effects on Plants 16
2.4 Effects on Materials 17
2.5 Environmental Air Standards 17

3. SOURCES 18

3.1 Natural Occurrence 18
3.2 Production Sources 19
3.2.1 Mines 19
3.2.2 Metallurgical Industry 19
3.3 Product Sources 20
3.4 Other Sources 23
3.4.1 Asbestos 23
3.4.2 Coal 23
3.4.3 Fuel Oil 24
3.4.4 Incineration 24
3.5 Environmental Air Concentration 25

4. ABATEMENT 27

5. ECONOMICS 28

6. METHODS OF ANALYSIS 29

6.1 Sampling Methods 29
6.2 Quantitative Methods 29
6.2.1 Nickel Particulates 29
6.2.2 Nickel Carbonyl 30

7. SUMMARY AND CONCLUSIONS 34

REFERENCES

APPENDIX

LIST OF TABLES

1. Cancer of the Respiratory Tract from Exposure to Nickel 7

2. Mortality in Ontario Nickel Refinery Workers, 1930-1957 10

3. Nickel in Coal 24

4. Emissions from Diesel Engine Exhaust 25

5. Mortality in Ontario Nickel Refinery Workers by Exposure Groups 1930-1965 46

6. Analysis of Flue Dust from Ontario Nickel Refinery 47

7. Nickel Concentration in the Organs of Mice Exposed to Nickel Carbonyl 48

8. Distribution of Nickel-63 in Rats 49

9. Production and Consumption of Nickel 50

10. Nickel (Exclusive of Scrap) Consumed in the United States, by Uses 51

11. Refiners or Processors of Nickel in the United States in 1963 52

12. Nickel in Coal Ash 53

13. Nickel Emissions from Coal-Fired Power Plants . . . 54

14. Average Concentrations of Suspended Particulates and Nickel at 30 Urban NASN Stations for the Periods 1957-1960 and 1961-1964 55

15. Nickel in the Atmosphere at Cincinnati and Indian Creek, 1967 56

16. Physical Properties of Nickel and Nickel Carbonyl 57

17. Animal Exposure to Nickel Carbonyl 58

18. Concentration of Nickel in the Air 60

19. Properties, Toxicity, and Uses of Nickel and Some Nickel Compounds 66

1. INTRODUCTION

Exposure in the working environment to nickel dust and vapors may have produced cancers of the lung and sinus, other disorders of the respiratory system, and dermatitis. Nickel dermatitis has also been observed in people who were not industrially exposed.

Nickel is a grayish-white metallic element—hard, tough, and markedly resistant to oxidation and corrosion—which forms a variety of alloys with other metals. The majority of the nickel produced is consumed in nickel alloys, particularly stainless steel. Nickel is also used extensively in catalysts, chemicals, and the nickel-plating process. Among the important volatile nickel chemicals are the organic complexes. These complexes are used as fuel additives for both aviation and automobile fuels. The most important nickel complex is nickel carbonyl, which is a demonstrated carcinogen.

The properties of nickel and its compounds are listed in Tables 16 and 19 in the Appendix.

2. EFFECTS

2.1 Effects on Humans

The toxicity of nickel and its compounds has been reviewed by Stokinger[90,91] and Mastromatteo.[68]

Airborne nickel may be inhaled or absorbed through the skin, and the resulting effects are largely dependent on the chemical form of the nickel. For example, nickel metal is relatively nontoxic, while most nickel salts are highly toxic, and nickel carbonyl ($Ni(CO)_4$) is extremely toxic. The effects produced may be dermatitis, respiratory disorders, or cancer of the respiratory system.[68,91]

Inhalation of nickel carbonyl may produce acute effects. Depending on the severity of the exposure, both initial and delayed symptoms may develop. Initial symptoms include dizziness and headache, often associated with dyspnea and vomiting, but generally these symptoms disappear when the individual is exposed to fresh air. Delayed symptoms may develop from 12 to 36 hours following exposure. Dyspnea returns, cyanosis appears, the temperature rises, and leukocytosis occurs. Delirium and other signs of central nervous system disturbance usually appear at this time. In some cases, the two stages may merge. Accidental exposures to high concentrations have resulted in an acute chemical pneumonitis, regardless of the time required for symptoms to develop. In fatal cases, death usually occurred between 4 and 11 days after the accidental exposure.[68,91,93]

2.1.1 Dermatitis

It has been known for some time that dermatitis results from contact with nickel-plated articles. Numerous cases of dermatitis have also been reported among workers engaged in refining nickel, and in electroplating with nickel. There are two aspects of nickel dermatitis—a simple dermatitis at the area of contact, and a chronic eczematous reaction which becomes more widespread. The typical "nickel itch" usually begins with a burning and itching of the exposed skin. Erythema occurs, and later a nodular eruption in the web of the fingers and in the forearms appears. These nodules may eventually form pustules. Recovery is common within one week after removal from exposure, but the rash may persist for weeks in some cases.[68]

Chamont and Himmelbach[27] report on investigations made on workers engaged in electroplating with chromium, nickel, copper, and zinc. Of 25 workers exposed to nickel, 7 suffered dermatosis in the form of papular erythema with intense itching, primarily on the forearms, but sometimes on the neck and eyelids. This skin condition disappeared when workers were on their annual vacations but recurred when they returned to work. The temperature at which the plating operation is carried out played an important part in sensitizing the workers to nickel: when the bath temperature was 60°C, the proportion of dermatosis was much greater than at 35° to 45°C.

Marcussen[66] reported that nickel dermatoses have been observed in occupations other than the plating industry. A Danish survey of 621 cases showed that 4 percent were due to nickel-plating, 9.5 percent to the use of nickel in other occupations, and 86.5 percent to contact with articles in everyday use. Articles mentioned frequently in this connection were nickel coins, nickel-plated jewelry, nickel-plated kitchen or medical utensils, and other nickel-plated items handled or used by cashiers, sales clerks, nurses, etc.

Watt and Vauman[110] observed 17 women who had become allergic to nickel after having their earlobes pierced. Drainage and eczematous reaction of the pierced lobes developed in all 17 within 2 to 6 weeks while they were wearing nickel-plated earrings. Ten of them subsequently developed more widespread reactions. Fifteen of the women had signs or symptoms of atopic diathesis.

Because of reports that patients who have an allergic dermatitis caused by metals are often allergic to more than one metal, Fregert and Rorseman[38] examined 5,416 patients suspected of having contact dermatitis. Patch tests were given to test the possibility of cross-sensitization among chromium, nickel, and cobalt. The investigation revealed that coexisting allergies to these metals are due to the presence of several allergenic metals in the sensitizing objects rather than to cross-sensitization. Seventy-seven

percent of the females were sensitive to nickel as opposed to 10 percent of the males. Similar results were observed by Pirila and Forstrom.[81]

2.1.2 Respiratory Disorders

Inhalation of nickel fumes and nickel carbonyl vapors has produced respiratory disturbances. Some respiratory effects have been reported among workers engaged in such operations as nickel-polishing, electroplating, nickel-cadmium battery manufacture, and welding. Cases of acute pneumonitis resulting from exposure to nickel fumes have been described. However, most of these reports are compounded by concomitant exposure to other substances.[68]

Investigations of the lungs of workers[10,11,16,21,60,78,93] who have suffered from accidental exposure to nickel carbonyl, and of experimental animals,[8,12,14,43,56,97] have shown that lesions occur primarily in the pulmonary alveoli. The alveolar lining cells become hypertrophied, with enlarged nuclei and nucleoli, and numerous mitoses. Associated findings include capillary congestion, focal hemorrhages, interstitial edema, interstitial cellular proliferation, and fibrinous intraalveolar exudate.

Hackett and Sunderman[44] have claimed that intravenous, intraperitoneal, and subcutaneous injections of nickel carbonyl in rats produce clinical and pathologic reactions that are virtually indistinguishable from those which develop after inhaling nickel carbonyl. Moreover, they suggest that the

pulmonary alveolus has been shown to be the target tissue regardless of the route of administration, and they claim that nickel carbonyl can cross the alveolar wall in either direction.

Hickey et al.,[46] in a statistical analysis of atmospheric concentrations of metals in relation to certain chronic diseases, observed positive correlations between nickel and nephritis ($r = 0.48$), diseases of the heart ($r = 0.44$), diseases of the cardiovascular system ($r = 0.30$), arteriosclerotic heart ($r = 0.39$), hypertensive heart ($r = 0.45$), diabetes ($r = 0.30$), and lung cancer ($r = 0.32$).

The incidence of respiratory disease in various cities has been compared with concentrations of particulates in the urban air by Dohan et al.[33] They found a positive correlation between the concentrations of nickel and the respiratory disease rates.

2.1.3 Cancer of the Respiratory Tract

An increase in the risk of contracting cancer of the lung and nose has long been considered the chronic effect of inhaling dust and fumes in a nickel refinery. The greater-than-expected incidence of lung and sinus cancer is well documented and is summarized in Table 1. Although nickel is suspected, the specific carcinogen or carcinogens are unknown at this time.

Because other metals are present in most industrial

TABLE 1

CANCER OF THE RESPIRATORY TRACT FROM EXPOSURE TO NICKEL

Year	Observation
1932	Bridge[22] reported 10 cases of cancer of the interior of the nose that had occurred in a nickel refinery in Wales using nickel carbonyl.
1937	Baader[13] announced a high incidence of pulmonary cancer in nickel workers.
1938	Amor[9] reported that 21 workers in a nickel and copper refining and extracting operation developed cancer of the respiratory tract.
1948	Barrett[15] cited 47 cases of nasal cancer and 72 of lung cancer in a Welsh nickel refinery.
1949	Ministry of Pensions, Great Britain, officially designated cancer of the respiratory tract in nickel workers as an industrial disease.[96]
1950	Loken[65] reported 82 cases of lung cancer in nickel workers in Norway.
1958	Morgan[77] reported 131 cases of lung cancer in Welsh nickel workers.
1958	Doll[34] reported 35.5 percent of all deaths among nickel workers in Glamorganshire to be due to cancer of the respiratory tract.
1958	Williams[113] reported a pathologic study of five cases of lung cancer in Welsh nickel workers.
1959	Sutherland[102] reported 54 deaths from cancer among nickel refinery workers in Ontario. The death rate from sinus cancer was 200 times greater than expected.

exposures of workmen to nickel, these metals have often been cited as the possible carcinogenic agents. Arsenic, particularly, has been cited as the carcinogen, although the causal relationship between arsenic and cancer has been questioned by several investigators. (See the companion report on the air pollution aspects of arsenic.) Amor[9] has stated his belief that arsenic was the etiologic agent of cancer of the respiratory tract in 21 workers engaged in extracting and refining nickel and copper. He reported 19 nasal cancers. However, Mastromatteo[68] implies that nickel is more likely to be the carcinogenic agent.

Similarly, Morgan[77] reported 61 cases of nasal cancer and 131 of lung cancer in 2,094 Welsh nickel refiners for the period 1923 to 1957. These workers, exposed to dusty operations, showed a higher incidence of respiratory cancer than workers exposed to gaseous nickel carbonyl. The authors considered cancer of the nose to be much more significant than cancer of the lung as a measure of the biologic effect of the vapors and dust. Morgan[77] stressed arsenic as the possible carcinogenic agent. In 1924, precautions were taken to remove arsenic from the operations. In addition, ventilation and dust control equipment were added, some equipment was modernized, and respirators were provided for workers in dusty areas.

In a study of the same Welsh refinery, Doll[34] noted that the hazard of nasal cancer was largely removed in 1924.

He observed that for the period 1948 to 1956, death from cancer of the nose was 150 times the expected number of deaths, and for cancer of the lung it was five times the expected number of deaths. No excess mortality was observed in workers less than 50 years of age.

Williams[113] supplemented the studies of Morgan and Doll. He examined the lungs of five men who had worked in the Welsh nickel refinery. His findings showed that four of the five men had pulmonary carcinoma (three squamous-cell and one alveolar-cell); the fifth worker had no cancer of the lung. Nickel (90 to 120 ppm)* and copper (460 to 2,810 ppm)* were present in excess in the lungs of two men, but no arsenic (less than 0.2 ppm)* was detected. He suggested that exposure to nickel and chronic inflammation were responsible for the carcinogenic action.

The exposure time and concentration of airborne nickel refinery dusts required to produce cancer is not known. However, Barrett,[15] in his annual report of nickel refineries in Great Britain, reported 47 cases of nasal cancer and 72 of lung cancer for the period 1923 to 1948. The average number of years worked before the occurrence of nasal and lung cancer was 23 and 25 years respectively. In 1950, Loken[65] reported three cases of lung cancer among workers in a Norwegian nickel refinery. All three had bronchogenic carcinomas and all had previously had pneumonectomies. One of

---

*Concentration of metal in dried lung.

these men, who had worked 10 years at a roasting furnace and then had been away from nickel for 8 years, showed (on examination of the lungs) localized fibrosis, asbestos bodies, and a high concentration of nickel in lungs (between 1,000 and 2,800 ppm).

Mastromatteo[68] has cited the unpublished study by Sutherland[102] of an Ontario nickel refinery, covering the period 1930 to 1957. In this study, 2,355 workers with 5 or more years of exposure were included. Table 2 summarizes the cause of death of 245 workers. All deaths between 1946 and 1957 from sinus cancer occurred in workers employed before 1934. Furnace workers with more than 3 years' exposure had a death rate 200 times higher than expected.

TABLE 2

MORTALITY IN ONTARIO NICKEL REFINERY WORKERS, 1930-1957[102]

Cause of Death	Number of Deaths	
	Observed	Expected
Sinus cancer	7	0.19
Pulmonary cancer	19	8.45
Cancer, all sites	54	43.19
Vascular lesions of central nervous system	14	20.72
Respiratory diseases	13	16.21
Gastrointestinal diseases	9	16.07
All causes	245	308

Sinter plant workers also showed an increased risk of death from sinus cancer. The study demonstrated that risk of

sinus cancer increased with the duration of furnace exposure. However, some evidence strongly suggested that exposure of less than 1 year at a cupola furnace may produce sinus cancer.[102]

The risk of death by lung cancer increased for anode furnace workers who were employed 25 years or more. The data suggested an increased risk (3.6 times that expected) after 3 years or more of furnace exposure. Increased risks of lung cancer were also noted with 6 months' exposure at cupola furnaces and 3 years or more of exposure at a sinter plant.[102]

The risk of lung cancer among nickel process workers was 2.25 times greater than expected.[102]

Mastromatteo[68] updated Sutherland's study[102] and observed an additional nine deaths from sinus cancer and 16 from lung cancer in the period 1958 to 1965. These data are summarized with Sutherland's data in Table 5 in the Appendix.

Analysis of flue dust from the Ontario nickel refinery shows the composition given in Table 6 (Appendix), with greater than 85 percent being nickel compounds. For this reason, Gilman[40] implanted into the thigh muscle of rats the following materials: nickel sulfide (Ni_3S_3), nickel oxide (NiO), nickel sulfate ($NiSO_4 \cdot 6H_2O$), cobalt sulfide (CoS), cobalt oxide (CoO), iron oxide (Fe_2O_3), copper oxide (CuO), and some of the flue dust from the refinery. Nickel sulfide, nickel oxide, cobalt sulfide, cobalt oxide, and the flue dust induced cancers, but no cancers were produced by the other substances. The sulfides induced a significantly higher

tumor incidence than did the oxides.

Sunderman, Sunderman Jr., and their co-workers[92-101] have exposed rats to nickel carbonyl (see Table 17 in the Appendix) and have subsequently shown that cancer of the respiratory tract can be induced. In some instances, a single exposure to 280,000 to 550,000 $\mu g/m^3$ (35-80 ppm*) produced an aplastic carcinoma. In less intense exposures of 28,000 $\mu g/m^3$ (4 ppm), either squamous-cell carcinoma or adenocarcinoma was produced in approximately 24 months.

Sunderman and Sunderman, Jr.[94] also suggest that nickel carbonyl—which is present in tobacco smoke—may be a carcinogen. They found 1.5 to 3.0 μg of nickel per cigarette in six common brands of American cigarettes.

There still remains some question as to the mechanism of damage by nickel carbonyl. Some investigators argue that the nickel carbonyl remains complexed as it attacks the alveolar cells. Others suggest that nickel carbonyl decomposes to produce finely divided nickel particles which affect the lungs in a different manner than the larger particles of nickel dust.[68]

2.2 Effects on Animals

2.2.1 Commercial and Domestic Animals

No evidence of damage to commercial or domestic animals by nickel air pollution was found. However, Weber and Reid[111] fed nickel acetate and nickel sulfate to growing chicks. When the concentration of nickel in the feed

*1 ppm = 6,900 $\mu g/m^3$; 1 $\mu g/m^3$ = 149 ppm at 25°C and 760 mm Hg.

exceeded 900 ppm, a progressive decrease in growth rate was observed.

2.2.2 Experimental Animals

2.2.2.1 Toxicity

Stokinger[91] reports that the toxicity of nickel depends largely on the chemical nature of the nickel compound and the mode of administration. For example, oral tolerance of nickel metal is relatively high, since dogs ingested 1 to 3 g/kg without effect. Daily doses of 4 to 12 mg/kg for 200 days produced no ill effects in either dogs or cats.

There is no evidence that nickel absorbed from food is of any health significance even though the food may absorb a few milligrams of nickel daily from nickel or nickel-alloy cookware.[91]

Nickel salts are highly toxic, particularly when they are administered intravenously or subcutaneously. Lethal doses of nickel salts administered subcutaneously are 7,000 to 8,000 μg/kg for rabbits and 9,000 to 16,000 μg/kg for cats. Dogs were found to die after single intravenous doses of 10,000 to 20,000 μg/kg of either nickel chloride or colloidal nickel.[68,91]

The toxicity of nickel carbonyl inhalation has been demonstrated by Sunderman and Kincaid.[93] Their data show that the LD_{50} values for 30 minutes' exposure for mice, rats, and cats are about 70,000, 240,000, and 1,890,000 $\mu g/m^3$ respectively.

The pathological effects of nickel in the body have also been studied. Hackett and Sunderman[44] showed that nickel carbonyl attacked the pulmonary alveolar cells regardless of the mode of exposure (see page 5).

Wase et al.,[109] using radioactive nickel, found that nickel complexes strongly with the lung protein. The reason for this affinity is not understood.

The quantity of nickel which accumulated in the organs of mice exposed to nickel carbonyl of low concentration (exact concentrations not given) was almost proportional to the frequency of exposure.[54] The data are given in Table 7 in the Appendix.

When radioactive nickel-63 was injected intravenously into rats by Smith and Hackley,[88] body tissues showed the distribution given in Table 8 (Appendix). Analyses showed that 60 percent of the nickel was excreted in the urine and less than 6 percent in the feces in 72 hours. As the authors point out, the route of excretion depends on the mode of administration. Ingested nickel is excreted primarily in the feces while inhaled nickel is excreted mainly in the urine. These results were supported by Imbus, et al.,[50] who reported that the nickel content excreted from 154 normal male workers averaged 7.6 µg/liter in the urine. Blood samples from the same workers averaged 3 µg/100 g. Morgan[77] reported the nickel content of urine to be 0.008 to 0.15 ppm in nickel carbonyl workers, 0.01 to 0.043 ppm in nickel smelter furnace

workers, 0.005 to 0.06 ppm in nickel chemical plant workers, and 0.002 to 0.05 ppm in nickel calcination plant workers. Only the nickel concentration in the urine of the nickel carbonyl workers was considered significantly above normal. Morgan pointed out that urinalyses alone cannot be used as an indication of nickel exposure.

Schroeder et al.[85,86] concluded that nickel had little or no effect on the mortality or growth of mice fed 5 ppm nickel (bivalent).

2.2.2.2 Carcinogenicity

The carcinogenic action of nickel carbonyl has been demonstrated through experimental exposure of animals. Some of the data are summarized in Table 17 in the Appendix.

After finely powdered nickel was injected intratracheally in rats by Hueper and Payne,[47,49] cancer was observed in 28 of 100 animals. Intrapulmonary deposition of the fine nickel dust produced only one sarcoma in 34 rats. In another experiment, rats and hamsters inhaled nickel powder and sulfur dioxide, but cancer was not induced.

In the U.S.S.R., nickel sinter dust containing 65 percent nickel sulfide and nickel oxide was administered to rats by inhalation and intratracheal injection; connective tissue nodules subsequently appeared. Electric furnace dust containing 95 percent nickel oxide administered to rats in the same manner produced a diffuse pulmonary sclerosis, but no tumors were induced.[17]

2.3 Effects on Plants

Although no information was found on the air pollution effects of nickel on vegetation, Lagerwerff[63] pointed out that plants have a lower tolerance to nickel than to lead and the addition of nickel compounds to gasolines should be looked upon with due concern. He also indicated that superphosphates containing nickel impurities have been the only known cause of soil contamination with this metal in the past.

Infertility of soil due to nickel as a native constituent is a problem in Scotland and Southern Rhodesia.

The toxicity of nickel to plants is inversely related to the pH of the soil. Application of lime, which can change the pH, has resulted in a reduction of toxic symptoms. For example, a 70 percent reduction in nickel uptake by sugar beets occurred when the soil pH was raised from 4.8 to 6.3 by liming.[63]

According to Tso,[108] very young tobacco seedlings are sensitive to nickel toxicity: some developed extensive brown necrosis and many died. Older seedlings in sand culture were seriously affected by a nutrient solution containing 2.5 ppm nickel.

Mizuno[60] studied the toxic effects of nickel on various plants. Fifteen common crops were studied, including kidney bean, soybean, adzuki bean, cabbage, alfalfa, timothy, potato, radish, oats, and corn. He also found that the degree of toxicity depended on the type of plant and the pH of the soil. The effect of nickel toxicity is manifested by necrotic

areas of chlorosis. He indicates that there is a correlation between nickel toxicity and the iron and copper content of the plant: (1) Plants with a ratio of copper to nickel of less than 1 had necrotic or chlorotic leaves, although the crop yield was not always decreased. (2) When the ratio of iron to nickel in the plants was less than 5, there was a decrease in the crop yield, although symptoms of necrosis or chlorosis did not develop. (3) In most of the plants there was a decrease in the crop yield at the same time as toxic symptoms developed, but it was unusual for the two phenomena to occur independently. (4) With a decrease in soil pH and the ratio of either iron to nickel, or copper to nickel, the plant's resistance to nickel was weak.

2.4 Effects on Materials

No information was found relating to the effects of airborne nickel or its compounds on materials. However, soiling and chemical staining may result from nickel particulates.

2.5 Environmental Air Standards

The American Conference of Governmental Industrial Hygienists[106] and the American Industrial Hygiene Association[79,80] have recommended an 8-hour threshold limit value for industrial workers of 7 $\mu g/m^3$ (0.001 ppm) for nickel carbonyl and 1,000 $\mu g/m^3$ for nickel metal or its soluble compounds.

3. SOURCES

3.1 Natural Occurrence

Although nickel is widely distributed over the face of the earth (about 0.016 percent in the earth's crust), the igneous rocks in which nickel occurs are not readily susceptible to concentration by weathering. Hence, there are relatively few workable deposits, and even in these the concentrations are usually so low that economic exploitation depends on the recovery of valuable by-products. Nickel minerals are most commonly sulfides, oxides, silicates, and arsenicals, the most important of which are the sulfides and oxides. Native nickel approaching purity is unknown. Small quantities of nickel combined with iron have been found in meteorites.[82]

The distribution of nickel in materials and animal and plant tissue was studied by Schroeder et al.[84] They found that nickel occurred in varying amounts in foods, water, sea water, animal tissues, and miscellaneous materials. The amount of nickel ranges from practically none to a few μg/g, depending on the material and its geographical location. These authors concluded that nickel is concentrated by certain foods, such as whole grains and legumes, which supply the nickel in the diet of some animals. A few processed foods and materials were apparently contaminated during their manufacture.

3.2 Production Sources

3.2.1 Mines

There are only a few deposits of nickel ore in the United States. Approximately 90 percent of nickel consumed in this country is imported from Canada. In the United States, the silicate and nickel-bearing ores near Riddle in Douglas County, Oreg.(Hanna Nickel Smelting Co.), are the source of the only appreciable production of nickel. Other locations of nickel ore in the United States are near Fredericktown, Mo.; the Lancaster Gap area in Pennsylvania; Lake County, Minn.; Grant County, N. Mex.; and Alaska.[82]

3.2.2 Metallurgical Industry

The Hanna Nickel Smelting Co. smelts garnierite ore by the d'Ugrine process. The ore is melted in electric furnaces to produce ferronickel.[73]

The production and consumption of nickel in the United States is compared with imports, exports, and world production in Table 9 (Appendix). The United States consumption is listed by use in Table 10 in the Appendix.

Nickel is imported in various forms, such as: (1) nickel pellets, produced by decomposition of nickel carbonyl (Mond process); (2) electrolytic cathode sheets cut into various sizes; (3) shot, obtained by remelting electrolytic nickel and then casting it without deoxidation; (4) malleable nickel, produced by pouring into ingot molds after deoxidation; (5) nickel rondelles, reduced from the oxide without fusion;

(6) nickel salts; (7) nickel oxide; (8) ferronickel; (9) nickel powder; and (10) special alloys for addition to cast irons.[82]

3.3 Product Sources

Nickel is used primarily in the metallurgical industry. Although stainless steels contain 3 to 35 percent nickel and some nickel alloys contain as much as 65 percent nickel,[82] Schueneman et al.[87] do not list any nickel in the particulate emissions from iron and steel furnaces. However, in Huntington, W. Va., the nickel concentration was 1.2 $\mu g/m^3$ near the Alloy Products Division of the International Nickel Co., Inc. This ambient air concentration was appreciably higher than the concentration (0.04 $\mu g/m^3$) at six other sampling stations in the Ironton-Ashland-Huntington Valley.[51]

A list of refiners and processors of nickel in the United States is given in Table 11 in the Appendix.

Nickel plating is used extensively to produce either a nickel-surfaced material or highly lustrous finishes such as those found on chrome-plated articles. Often an undercoat of copper is employed to create a better surface for the deposition of nickel. The nickel coatings may be produced by a number of processes: electroplating, electroless plating (chemical plating), electroforming (nickel cast on a mold), nickel cladding (pressure welding), spraying (usually powdered nickel sprayed on metal and fused), and vapor-deposited coatings (chemical vapor deposition by thermal or chemical decomposition of nickel carbonyl, nickel acetyl acetonate, or nickel

chloride).[82] Although nickel platers have been observed to develop deleterious health effects from apparent exposure to nickel particulates or mists, no information was found on the emission rates of nickel from plating facilities.

Nickel carbonyl is used to produce powdered nickel, which is used extensively in powder metallurgy. The nickel carbonyl-produced powder is particularly suited for this process because it is fine and of irregular particle size.[26,82]

Nickel is used extensively as a catalyst. The nickel catalyst which is used most frequently is Raney nickel. This special type of catalyst is prepared from intermetallic compounds, such as $NiAl_3$, by dissolution of the other metal in caustic solutions. Among the applications of nickel catalysts are hydrogenation of organic compounds, dehydrogenation of organic compounds, artificial aging of liquors, drying of oils, bleaching, purification of waste water, removal of organic sulfur compounds from coal gas, manufacture of alcohol from gas oil, cracking of ammonia, manufacture of hydrazine from urea, and catalytic combustion of organic compounds in auto exhaust.[82]

Nickel carbonyl and other zerovalent nickel compounds are used as catalysts for carbonylation, polymerization, and miscellaneous reactions.[57] Nickel carbonyl is used extensively as the catalyst in the carbonylation of acetylene to acrylic acid. The nickel carbonyl is prepared from nickel chloride and stored by refrigeration under an atmosphere of

carbon monoxide. Exhaust gases from the production and use of nickel carbonyl are passed through a decontamination furnace, where the gases are heated to destroy the nickel carbonyl.

Nickel complexes have been patented for use as fuel additives. One of the earliest to be patented was nickel carbonyl ($Ni(CO)_4$) for supercharged aviation fuels.[53] Some cyclopentadienyl nickel complexes claimed as fuel additives include cyclopentadienyl-nickelnitrosyl,[24] dicyclopentadienyl-nickelalkynes,[35] and bis(cyclopentadienylnickel)alkynes.[36] Nickel isodecylorthophosphate reportedly increases engine performance and reduces wear.[52] Nickel chelates of salicyl-aldehyde nitrites have been claimed to minimize carbon deposits.[72] Complexes with β-diketones, such as acetyl-acetonate, have been reported to eliminate carbon deposits and to improve lubrication and combustion.[52]

Even though nickel carbonyl is extremely toxic, it is used extensively as an intermediate product in the Mond process of refining nickel. Carbon monoxide gas is passed over powdered nickel at approximately 50°C. Gaseous nickel carbonyl formed is then passed through a furnace, where it is heated above 60°C and the complex decomposes to give a high-purity nickel powder.[82] Brief et al.[23] have studied the potential for formation of nickel carbonyl. Their data indicate that nickel carbonyl can be formed in significant

concentrations (at 25°C) any time the concentration of carbon monoxide exceeds 100 ppm in the presence of finely divided nickel. As a result, nickel carbonyl has been produced in unexpected places. For example, gases containing some carbon monoxide were found to contain nickel carbonyl after passing through nickel-alloyed pipes.

3.4 Other Sources

3.4.1 Asbestos

Some investigators[29,30,32,42,45] have suggested that the small amounts of nickel or other trace substances found in asbestos may be the cause of cancer associated with asbestos. The nickel concentration in the most common asbestos mineral, chrysolite, was found to range from approximately 1,500 to 1,800 µg/g.[22]

3.4.2 Coal

The concentration of nickel in coal ash varies from 3 to 10,000 µg/g, depending on the origin of the coal.[1] The nickel contents of some selected coal ashes are given in Table 12 (Appendix). The nickel emissions of six different types of coal-fired power plants are given in Table 13 (Appendix).

Given[41] reported finding 110 ppm nickel in crude oil and 100 to 150 ppm as the average crustal abundance of nickel in Western coal. He also reported the concentration of nickel in coal as follows:

TABLE 3

NICKEL IN COAL*[41]

Field	Nickel (ppm)
Iowa, Missouri, Northern Oklahoma	2-42
Southern Oklahoma	0-15
Arkansas	4-20
Illinois	3-22

*Variations in weathered and nonweathered samples of coal were as high as 11 to 95 ppm nickel respectively.

3.4.3 Fuel Oil

Fly ash from residual fuel oil has been found to contain small amounts of nickel, usually as nickel oxide. Two tests burning Pacific Standard 400 oil and 4° API (American Petroleum Institute) resulted in 1.8 and 13.2 percent nickel oxide (NiO) respectively in the fly ash.[89]

Boldt[20] reported the concentration of nickel in oil.* Crude oil contained 55 μg/g of nickel, while the asphaltene fraction contained 245 μg/g.

Emissions from diesel engine exhaust have been analyzed by Frey and Corn.[39] The results in relation to nickel are presented in Table 4.

3.4.4 Incineration

Analyses of particulate emissions from municipal incinerators in Milwaukee showed that the ash contained 1 to 10 percent nickel.[28]

*Tatums Field, Carter County, Okla.

TABLE 4

EMISSIONS FROM DIESEL ENGINE[a] EXHAUST[39]

Substances	Nickel Concentration
Bulk diesel fuel[b]	2 µg/g
Exhaust valve coke	10 µg/g
Particulate sample[c]	10,000 µg/g (0.65 µg/min)
Particulate sample[d]	1,000 µg/g
Particulate sample[e]	500 µg/g

[a] 1 cylinder American Marc, Inc. (Model AC 1).
[b] New York Central Specification No. 1370-C, Grade 2.
[c] No load at 1,400 rpm.
[d] No load at 1,800 rpm.
[e] Half load at 1,800 rpm.

3.5 Environmental Air Concentrations

Air quality data on nickel obtained from the National Air Sampling Network are shown in Table 18 in the Appendix. In 1964 the national average concentration of nickel from 103 sampling stations of the network was 0.032 µg/m^3, while the national maximum concentration was 0.690 µg/m^3 in East Chicago, Ind. [2,4,5,6] However, the concentration of nickel measured in Huntington, W. Va.,[51] during a special survey (see page 20) was 1.2 µg/m^3, which was over twice as high as the national maximum.

McMullen[70] averaged the nickel concentrations from the National Air Sampling Network for the two 4-year periods

1957 to 1960 and 1961 to 1964. He observed that nickel concentrations in suspended particulates from 30 urban stations (Table 14, Appendix) averaged 0.045 $\mu g/m^3$ in the first period and 0.035 $\mu g/m^3$ in the later period—a decrease of 22 percent. However, over the same two time periods the suspended particulate decreased 12 percent. Considering nickel alone, he concluded that the reduction was significant; but considering the nickel as a fraction of the particulate, the reduction in nickel was not statistically significant.

In a statistical analysis of metals found in the lungs of adult males, Tipton and Shafer[107] concluded that the nickel concentration in lungs was significantly higher in Seattle than in Baltimore, Dallas, Denver, Miami, Richmond, and San Francisco.

Comparisons of atmospheric data from Cincinnati, Ohio, and a rural area show that city nickel concentrations were twice as high as rural concentrations (Table 15, Appendix).[64]

4. ABATEMENT

Nickel air pollution usually occurs as particulate emissions and may be controlled with the particulate by the usual dust handling equipment such as bag filters, precipitators, and scrubbers.[20] Nickel poses no unique control problems except with gaseous nickel carbonyl. Control of nickel carbonyl is accomplished by taking advantage of the fact that nickel carbonyl decomposes at temperatures above 60°C. For this reason gases containing nickel carbonyl are usually passed through a furnace, where the nickel carbonyl decomposes into its two components, nickel and carbon monoxide. The resulting nickel metal can then be removed as particulate.[57] No control methods were found for nickel emissions from vehicle engine exhausts.

5. ECONOMICS

No information has been found on the economic costs of nickel air pollution or on the costs of its abatement.

The production and consumption data for nickel have been discussed in Section 3.

6. METHODS OF ANALYSIS

6.1 Sampling Methods

Dusts and fumes of nickel compounds may be collected by any method suitable for collection of other dusts and fumes: the impinger, electrostatic precipitator, and filters are commonly used. The National Air Sampling Network uses a high-volume filtration sampler.[3] The sampling of $Ni(CO)_4$ requires a special sampling solution, and various sampling techniques are discussed with the quantitative methods.

6.2 Quantitative Methods

6.2.1 Nickel Particulates

Emission spectroscopy has been used by the National Air Pollution Control Administration for nickel analysis of samples from the National Air Sampling Network.[3,105] The samples are ashed and extracted to eliminate interfering elements. The minimum detectable nickel concentration by emission spectroscopy is 0.0064 $\mu g/m^3$ for urban samples and 0.0016 $\mu g/m^3$ for nonurban samples. The different sensitivities result from different extraction procedures required for urban samples.[3]

Thompson *et al.*[105] have reported that the National Air Pollution Control Administration uses atomic absorption to supplement analyses obtained by emission spectroscopy. The method has a minimum detectable limit of 0.004 $\mu g/m^3$, based on a 2,000 m^3 air sample.

The ring-oven technique has been adapted to the measurement of nickel particulates. Dimethylglyoxime is used as the coloring agent. The lower limit of identification is 0.08 μg, and the normal range of measurement is 0.10 to 1.0 μg.[112]

In addition to the above test, a number of colorimetric procedures, all using dimethylglyoxime, have been described for the detection of nickel.[37,55,58,61,67,103]

6.2.2 Nickel Carbonyl

Brief et al.[23] mention five methods which have been used for the determination of nickel carbonyl:

(1) An air sample can be bubbled through a saturated solution of sulfur in trifluoroethylene. The sulfur reacts with nickel to form a precipitate. Spectrographic examination is sensitive to 0.0003 ppm nickel carbonyl.

(2) An air sample may be drawn through a tube containing red mercuric oxide at 200°C and the liberated mercury may be determined spectrographically. A parallel stream of air is drawn through an oxidizing reagent to convert the CO to CO_2, and the stream is passed over mercuric oxide; the liberated mercury is again determined spectrographically. The difference in the amounts of mercury vapor measured corresponds to the nickel carbonyl content in the air. A sensitivity of 0.0014 ppm is reported.

(3) The nickel carbonyl may be absorbed in chloramine-B. The nickel determination is accomplished colorimetrically using

dimethylglyoxime. For a 30-minute sample, at the suggested sampling rate of 0.5 liter per minute, a sensitivity of 0.01 ppm is obtained.

(4) Another colorimetric method uses iodine in carbon tetrachloride as the collection medium. The nickel is colored with dimethylglyoxime. A sensitivity of 0.1 ppm to nickel carbonyl is claimed.

(5) Nickel carbonyl may be collected in dilute sulfuric acid followed by spectrophotometry using sodium diethyldithiocarbamate as the coloring agent.

Brief et al.[23] collected a sample in dilute hydrochloric acid in a midget impinger (0.1 cfm* for 30 minutes). The nickel was complexed with alpha-furildioxime and extracted with chloroform. The nickel content is determined spectrophotometrically, and the method is sensitive to 0.0008 ppm.

The American Industrial Hygiene Association indicates[80] that a direct field instrument is commercially available. This instrument is useful for continuous monitoring of operations involving nickel carbonyl. The instrument can detect concentrations as low as 10 ppb and as high as 1,500 ppb.

Another field method has been described by Kobayashi.[59] Air is drawn through a tube filled with silica gel impregnated with 0.5 percent gold chloride. In the presence of nickel carbonyl, the silica gel changes from a light yellow to bluish-violet. The concentration of nickel carbonyl

*Cubic feet per minute.

is a function of the length of the colored layer. The useful range of a 100-cc sample is 200 to 600 ppm. By measuring the minimum volume of test gas needed to color the silica gel at a constant sampling rate, the concentration of nickel carbonyl—down to 3 ppm—can be determined.

In another method,[18] the test air is drawn at 0.5 liter per minute through an absorption tube containing one or two 15 mm diameter filter papers and then through two absorption vessels with porous plates. Each plate contains 3 ml of a 1.5 percent solution of chloramine B in alcohol. The chloramine B solution retains the nickel carbonyl vapor. The colored vapor is compared with standards. The sensitivity of the method is 1 μg of nickel carbonyl; the error does not exceed 10 percent.

Sunderman *et al.*[101] have developed a gas chromatographic method for the detection of nickel carbonyl in the blood and breath. A carbowax 20 M column and electron capture detector were used.

McCarley *et al.*[69] describe a continuous monitor of nickel carbonyl. Polarized light is used to detect nickel carbonyl deposited on borosilicate glass. Concentrations in the range of 0.05 to 4 ppm can be measured.

Bergmann *et al.*[19] reported an X-ray fluorescence method for the determination of nickel in petroleum feed stocks. They claim a limit of detection of 0.05 μg of nickel per 10 g of feed stock.

An atomic absorption method for determining nickel in biological materials has been reported by Sunderman.[99] The nickel is extracted with dimethylglyoxime. This method permits measurement of the nickel levels in normal tissue or urine.

7. SUMMARY AND CONCLUSIONS

Nickel and its compounds are of concern as air pollutants because harmful effects of exposure to these materials have been observed among industrial workers. Exposure to airborne nickel dust and vapors may have produced cancers of the lung and sinus, other disorders of the respiratory system, and dermatitis. There is a substantially higher mortality rate among nickel workers due to sinus cancer—up to 200 times the expected number of deaths. However, since other metal dusts have also been present in industrial exposures to nickel, it has not been possible to determine whether nickel is the carcinogen. Yet experiments have shown that nickel carbonyl and nickel dusts can induce cancer in animals. Nickel contact dermatitis was found in 77 percent of the females and 10 percent of the males suspected of having allergenic reactions to metals. No information on the effects of nickel air pollution on commercial and domestic animals, plants, or materials was found in the literature.

The most likely sources of nickel in the air appear to be emissions from metallurgical plants using nickel, engines burning fuels containing nickel additives, and plating plants, as well as from the burning of coal and oil, and the incineration of nickel products. In 1964, urban air concentrations of nickel averaged 0.032 $\mu g/m^3$ and ranged up to a miximum of 0.690 $\mu g/m^3$ in East Chicago, Ind.

Emission of nickel in particulate form can be controlled

using normal control devices, such as precipitators, baghouses, and scrubbers. Nickel carbonyl, which is gaseous, must first be decomposed by heat before it is removed as a particulate.

No information has been found on the economic costs of nickel air pollution or on the costs of its abatement.

Methods of analysis are available which can be used to detect nickel at the 0.0064 $\mu g/m^3$ level and nickel carbonyl at the 7 $\mu g/m^3$ level.

Based on the material presented in this report, further studies are suggested in the following areas:

(1) Determination of the chemical composition of nickel compounds in the atmosphere. Measurement of the concentration of nickel near suspected sources, including metallurgical plants; vehicles' exhausts; and coal and oil-burning, plating, and incineration facilities. Measurement and analysis of the concentration of nickel in the emissions from these sources.

(2) Determination of the effect of nickel air pollution on plants and animals.

REFERENCES

1. Abernethy, R. F., and F. H. Gibson, Rare Elements in Coal, Bur. Mines Inform. Circ. IC-8163 (1963).

2. Air Pollution Measurements of the National Air Sampling Network, Analyses of Suspended Particulate Samples Collected 1953-1957, U.S. Public Health Serv. Publ. 637 (1958).

3. Air Pollution Measurements of the National Air Sampling Network—Analyses of Suspended Particulates, 1957-1961, U.S. Public Health Serv. Publ. 978 (1962).

4. Air Pollution Measurements of the National Air Sampling Network, Analyses of Suspended Particulates 1963. U.S. Dept. of Health, Education, and Welfare, Public Health Service, Cincinnati, Ohio (1965).

5. Air Quality Data, 1962, National Air Sampling Network, U.S. Dept. of Health, Education, and Welfare, Public Health Service, Cincinnati, Ohio.

6. Air Quality Data from the National Air Sampling Networks and Contributing State and Local Networks, 1964-1965, U.S. Dept. of Health, Education, and Welfare, Public Health Service, Division of Air Pollution, Cincinnati, Ohio (1966).

7. Air Quality Data from the National Air Sampling Networks and Contributing State and Local Networks, 1966 ed., U.S. Dept. of Health, Education, and Welfare, National Air Pollution Control Administration Publication No. APTD 68-9, U.S. Govt. Printing Office, Washington, D.C. (1968).

8. Amor, A. J., The Toxicology of the Carbonyls, J. Ind. Hyg. 14:216 (1932).

9. Amor, A. J., Bericht uber den VIII Internationalen Kongress fur Unfallmedizin und Berufskrankheiten. Frankfurt am Main. Sept. 26-30, 1938, Band 2 (Leipzig: Georg Thieme, p. 941, 1939).

10. Amor, A. J., cited by O. Bayer: Bericht uber einen Todesfall an Nickelkarbonyl-Vergiftung, Arch. Gewerbepathol. Gewerbehyg. 9:592 (1939).

11. Armit, H. W., The Toxicology of Nickel Carbonyl. Part I, J. Hyg. 7:525 (1907).

12. Armit, H. W., The Toxicology of Nickel Carbonyl. Part II, J. Hyg. 8:565 (1908).

13. Baader, E. W., in Berufskrebs—Neuere Ergebnisse auf dem Gebiete der Krebskrankheiten (Leipzig: S. Hirzel, pp. 116-117, 1937).

14. Barnes, J. M., and F. A. Denz, Effect of 2-3 Dimercapto-Propanol (BAL) on Experimental Nickel Carbonyl Poisoning, Brit. J. Ind. Med. 8:117 (1951).

15. Barrett, G. P., Annual Report of the Chief Inspector of Factories for the Year 1948 (London: Her Majesty's Stat. Off., p. 158, 1949).

16. Bayer, O., Beitrage zur Toxikologie, Klinik und pathologischen Anatomie der Nickelkarbonylvergiftung, Arch. Gewerbepathol. Gewerbehyg. 9:592 (1939).

17. Belobragina, G. V., and A. V. Saknyn, An Experimental Study Into the Effects Produced by Dust in the Nickel Industry, Gigiena. Truda i Prof. Zabolevaniya 7:8 (1962); (Abst.) Bull Hyg. 39:497 (1964).

18. Belyakov, A. A., The Determination of Microgram Quantities of Nickel, Nickel Tetracarbonyl, and its Solid Decomposition Products in Air, Zavodsk. Lab. 26:158 (1960).

19. Bergman, J. G., et al., Determination of Sub-Ppm Nickel and Vanadium in Petroleum by Ion Exchange Concentration and X-Ray Fluorescence, Anal. Chem. 39:1259 (1967).

20. Boldt, J. R., Jr., The Winning of Nickel. (Toronto: Longmans Canada Limited, 1967).

21. Brances, W. W., Nickel Carbonyl Poisoning Report of Case, J. Am. Med. Assoc. 102:1204 (1934).

22. Bridge, J. C., Annual Report of the Chief Inspector of Factories and Workshops for the Year 1932 (London: Her Majesty's Stat. Off., 1939.

23. Brief, R. S., F. S. Venable, and R. S. Ajemian, Nickel Carbonyl: Its Detection and Potential for Formation, Am. Ind. Hyg. Assoc. J. 26:72 (1965).

24. Brown, T., et al., U.S. Patent 3,249,964 (To Ethyl Corp., 1966).

25. Campbell, J. A., Lung Tumors in Mice and Man, Brit. Med. J. 2:179 (1943).

26. Carbonyl Nickel Power. Essential Alloying Element of P/M Steels, Nickel Topics 21(5):6 (1968).

27. Chamont, A. J., and J. J. Himmelbach, Professional Dermatosis due to Nickel, Berufsdermatosen 9:316 (1961).

28. Chass, R. L., and A. H. Rose, Discharge from Municipal Incinerators, Preprint, presented at the 46th Annual Meeting, Air Pollution Control Association (1953).

29. Cralley, L. J., et al., Characterization and Solubility of Metals Associated with Asbestos Fibers, Am. Ind. Hyg. Assoc. J. 29:569 (1968).

30. Cralley, L. J., R. G. Keenan, and J. R. Lynch, Exposure to Metals in the Manufacture of Asbestos Textile Products, Am. Ind. Hyg. Assoc. J. 28(5):452 (1967).

31. Cuffe, S. T., and R. W. Gerstle, Emissions from Coal-Fired Power Plants: A Comprehensive Summary, U.S. Dept. of Health, Education, and Welfare, Public Health Service, Bureau of Disease Prevention and Environmental Control, Cincinnati, Ohio (1967).

32. Cuthbert, J., The Community Hazards of Asbestos, Muench. Med. Wochschr. (Munich) 109:1369 (1967).

33. Dohan, F. C., G. S. Everts, and R. Smith, Variations in Air Pollution and the Incidence of Respiratory Disease, presented at the 55th Annual Meeting of the Air Pollution Control Association, Sheraton-Chicago Hotel, Chicago, Ill. (May 20-24, 1962).

34. Doll, R., Cancer of the Lung and Nose in Nickel Workers, Brit. J. Ind. Med. 15:224 (1958).

35. Dubeck, M., U.S. Patent 3,244,492 (To Ethyl Corp., 1966).

36. Dubeck, M., U.S. Patent 3,246,966 (To Ethyl Corp., 1966).

37. Feigl, F., and R. Stern, The Application of Spot Reactions in Qualitative Analysis, Z. Anal. Chem. 60:1 (1921).

38. Fregert, S., and H. Rorseman, Allergy to Chromium, Nickel, and Cobalt, Arch. Dermatol. Venereol. 46:144 (1966).

39. Frey, J. W., and M. Corn, Physical and Chemical Characteristics of Particulates in a Diesel Exhaust, Am. Ind. Assoc. J. 28(5):468 (1967).

40. Gilman, J. P. W., Metal Carcinogenesis. II. A Study on the Carcinogenic Activity of Cobalt, Copper, Iron and Nickel Compounds, Cancer Res. 22:158 (1962).

41. Given, P. H., Coal Science, Advan. Chem. Ser. 55 (1966).

42. Gross, P., et al., Experimental Asbestosis: The Development of Lung Cancer in Rats with Pulmonary Deposits of Chrysotile Asbestos Dust, Arch. Environ. Health 15(3): 343 (1967).

43. Hackett, R. L, and F. W. Sunderman, Jr., Acute Pathological Reactions to Administration of Nickel Carbonyl, Arch. Environ. Health 14:604 (1967).

44. Hackett, R. L. and F. W. Sunderman, Jr., Pulmonary Alveolar Reaction to Nickel Carbonyl. Ultrastructural and Histochemical Studies, Arch. Environ. Health 16:349 (1968).

45. Harington, J. S., Chemical Studies of Asbestos, Ann. N.Y. Acad. Sci. 132:31 (1965).

46. Hickey, R. J., E. P. Schoff, and R. C. Clelland, Relationship Between Air Pollution and Certain Chronic Disease Death Rates. Multivariate Statistical Studies, Arch. Environ. Health 15:728 (1967).

47. Hueper, W. C., Experimental Studies in Metal Cancerigenesis. IV. Cancer Produced by Parenterally Introduced Metallic Nickel, J. Natl. Cancer Inst. 16(1):55 (1955).

48. Hueper, W. C., Experimental Studies in Metal Carcinogenesis. IX. Pulmonary Lesions in Guinea Pigs and Rats Exposed to Prolonged Inhalation of Powdered Metallic Nickel, A.M.A. Arch. Pathol. 65:600 (1958).

49. Hueper, W. C., and W. W. Payne, Experimental Studies in Metal Carcinogenesis: Chromium, Nickel, Iron, Arsenic, Arch. Environ. Health 5:445 (1962).

50. Imbus, H. R., et al., Boron, Cadmium, Chromium and Nickel in the Blood and Urine, Arch. Environ. Health 6:286 (1963).

51. Ironton, Ohio—Ashland, Kentucky—Huntington, West Virginia—Air Pollution Abatement Activity, Pre-Conference Investigations, U.S. Dept. of Health, Education, and Welfare, Public Health Service (1968).

52. Italian Patent 527,990 (To WSSPA, CA 52:21039e, 1955).

53. Johnson, E., U.S. Patent 2,406,544 (To Texaco, Inc., 1946).

54. Kawase, H., Studies on the Prevention of Experimental Nickelcarbonyl Poisoning, Japan J. Ind. Health (Tokyo) 1(3):202 (June 1959).

55. Kielczewski, W., and J. Supinski, Determination of Microgram Quantities of Nickel by the Impregnated-Paper Method, Chem. Anal. (Warsaw), 10(4):677 (1965).

56. Kincaid, J. F., J. S. Strong, and F. W. Sunderman, Nickel Poisoning: I. Experimental Study of the Effects of Acute and Subacute Exposure to Nickel Carbonyl, Arch. Ind. Hyg. 8:48 (1953).

57. Kirk, R. E., and D. F. Othmer, "Nickel and Nickel Alloys," in Encyclopedia of Chemical Technology, vol. 13, 2nd ed. (New York: Interscience, pp. 735-753, 1967).

58. Kobayashi, Y., A Rapid Determination of a Small Amount of Nickel by Means of a Detector Tube, J. Chem. Soc. Japan, Ind. Chem. Sect. 58(10):728 (1955).

59. Kobayashi, Y., Rapid Method for the Determination of Low Concentrations of Nickel Carbonyl Vapor, Yuki Gosei Kagaku Kyokai Shi 15:466 (1957).

60. Krafft, K., "Nickelkarbonylpneumonien," in Berichte uber den VIII. Internationalen Kongress fur Unfallmedizin and Berufskrankheiten, vol. 2 (Leipzig: G. Theme Verlag, pp. 1054-1056, 1939).

61. Kutzelnigg, A., New Reagent Papers for Porosity Testing and for the Determination of Metals, Metalloberflaeche 5: B 113 (1951).

62. Kuz'Micheva, M. N., Determination of Vanadium in Air, Hyg. Sanitation (Gigiena i Sanit.) 31(2):216 (1966).

63. Lagerwerff, J. V., Heavy-Metal Contamination of Soils, Preprint. Soil and Water Conservation Research Division, Agricultural Research Service, U.S. Dept. of Agriculture, Beltsville, Maryland (1967).

64. Lee, R. E., Jr., R. K. Patterson, and J. Wagman, Concentration and Particle Size Distribution of Metals in Urban and Rural Air, Preprint, U.S. Dept. of Health, Education, and Welfare, National Air Pollution Control Administration, Cincinnati, Ohio (1969).

65. Loken, A. C., Lung Cancer in Nickel Workers, Tidsskr. Norske Laegeforen 70:376 (1950).

66. Marcussen, P. V., Ecological Considerations on Nickel Dermatitis, Brit. J. Ind. Med. 17:65 (1960).

67. Marion, S. P., and I. Zlochower, A Spot Test Analysis of the Group III Cations, J. Chem. Educ. 36:378 (1959).

68. Mastromatteo, E., Nickel: A Review of Its Occupational Health Aspects, J. Occupational Med. 9(3):127 (1967).

69. McCarley, J. E., R. S. Saltzman, and R. H. Osborn, Recording Nickel Carbonyl Detector, Anal. Chem. 28:880 (1956).

70. McMullen, T. B., Concentrations of Nickel in Urban Atmosphere (1957-1964), Preprint (1966).

71. The Merck Index, 8th ed. (Rahway, N.J.: Merck, 1968).

72. Miedzielski, E., U.S. Patent 2,891,853 (to E. I. duPont de Nemours & Co., Inc., 1959).

73. Mineral Facts and Problems. Bureau of Mines Bull. 630, U.S. Govt. Printing Office, Washington, D.C. (1965).

74. Minerals Yearbook, Bureau of Mines, Govt. Printing Office, Washington, D.C. (1966).

75. Minerals Yearbook, Bureau of Mines, Govt. Printing Office, Washington, D.C. (1967).

76. Mizuno, N., Interaction Between Iron and Nickel and Copper and Nickel in Various Plant Species, Nature 219:1271 (1968).

77. Morgan, J. G., Some Observations of the Incidence of Respiratory Cancer in Nickel Workers, Brit. J. Ind. Med. 15: 224 (1958).

78. Mott, F. W., Carbon Monoxide and Nickel Carbonyl Poisoning, Arch. Neurol. 3:246 (1907).

79. Nickel, Hygienic Guide Series, Am. Ind. Hyg. Assoc. J. 27(2):202 (1966).

80. Nickel Carbonyl, Hygienic Guide Series, Am. Ind. Hyg. Assoc. J. 29:304 (1968).

81. Pirila, V., and L. Forstrom, Pseudo-Cross-Sensitivity Between Cobalt and Nickel, Acta Dermato-Venereol. (Stockholm) 46(1):40-5 (1966).

82. Rosenburg, S. J., Nickel and Its Alloys, Nat. Bur. Std. (U.S.) Monograph 106 (May 1968).

83. Schoen, W. F., and R. L. Pontius, Soc. Automotive Engrs. J. 73(11):62 (1965).

84. Schroeder, H. A., J. J. Balassa, and I. H. Tipton, Abnormal Trace Metals in Man—Nickel, J. Chronic Diseases 15:51 (1962).

85. Schroeder, H. A., J. J. Balassa, and W. H. Vinton, Jr., Chromium, Lead, Cadmium, Nickel and Titanium in Mice: Effect on Mortality, Tumors and Tissue Levels, J. Nutr. 83(3):239 (1964).

86. Schroeder, H. A., W. H. Vinton, Jr., and J. J. Balassa, Effect of Chromium, Cadmium and Other Trace Metals on the Growth and Survival of Mice, J. Nutr. 80(1):39 (1963).

87. Shueneman, J. J., M. D. High, and W. E. Bye, Air Pollution Aspects of the Iron and Steel Industry, U.S. Dept. of Health, Education, and Welfare, Public Health Service, Division of Air Pollution, Cincinnati, Ohio (June 1963).

88. Smith, J. C., and B. Hackley, Distribution and Excretion of Nickel-63 Administered to Rats, J. Nutr. 95:541 (1968).

89. Smith, W. S., Atmospheric Emissions from Fuel Oil Combustion—An Inventory Guide, U.S. Dept. of Health, Education, and Welfare, Public Health Serv. Publ. 999-AP-2 (1962).

90. Stokinger, H. E., "Metal Carbonyls, $Me_x(CO)_y$," in Industrial Hygiene and Toxicology, vol. II, 2nd ed., F. A. Patty, Ed. (New York: Interscience, 1963).

91. Stokinger, H. E., "Nickel, Ni," in Industrial Hygiene and Toxicology, vol. II, 2nd ed., F. A. Patty, Ed. (New York: Interscience, 1963).

92. Sunderman, F. W., and A. J. Donnelly, Studies of Nickel Carcinogenesis Metastasizing Pulmonary Tumors in Rats Induced by the Inhalation of Nickel Carbonyl, Am. J. Pathol. 46(6):1027-41 (1965).

93. Sunderman, F. W., and J. F. Kincaid, Nickel Poisoning II. Studies of Patients Suffering from Acute Exposure to Vapors of Nickel Carbonyl, J. Am. Med. Assoc. 155:889 (1954).

94. Sunderman, F. W., and F. W. Sunderman, Jr., Nickel Poisoning. XI. Implication of Nickel as a Pulmonary Carcinogen in Tobacco Smoke, Am. J. Clin. Pathol. 35(3): 203 (1961).

95. Sunderman, F. W., et al., Nickel Poisoning. IV. Chronic Exposures of Rats to Nickel Carbonyl; A Report After One Year Observation, Arch. Ind. Hyg. 16:480 (1957).

96. Sunderman, F. W., et al., Nickel Poisoning. IX. Carcinogenesis in Rats Exposed to Nickel Carbonyl, Arch. Ind. Hyg. 20:36 (1959).

97. Sunderman, F. W., et al., Nickel Poisoning. XII. Metabolic and Pathologic Changes in Acute Pneumonitis from Nickel Carbonyl, Am. J. Clin. Pathol. 36:477 (1961).

98. Sunderman, F. W., Jr., Studies of Nickel Carcinogenesis: Alterations of Ribonucleic Acid Following Inhalation of Nickel Carbonyl, Am. J. Clin. Pathol. 39(6):549 (1963).

99. Sunderman, F. W., Jr., Measurements of Nickel in Biological Materials by Atomic Absorption Spectroscopy, Am. J. Clin. Pathol. 44(2):182 (1965).

100. Sunderman, F. W., Jr., and F. W. Sunderman, Studies on Nickel Carcinogenesis. The Subcellular Partition of Nickel in Lung and Liver Following Inhalation of Nickel Carbonyl, Am. J. Clin. Pathol. 40(6):563 (1963).

101. Sunderman, F. W., Jr., N. O. Roszel, and R. J. Clark, Gas Chromatography of Nickel Carbonyl in Blood and Breath, Arch. Environ. Health 16:836 (1968).

102. Sutherland, R. B., Respiratory Cancer Mortality in Workers Employed in an Ontario Nickel Refinery Covering the Period 1930 to 1957, Division of Industrial Hygiene, Ontario Department of Health. Unpublished report, Nov. 1959, with additions.

103. Tananaev, N. A., Qualitative Analysis of the Elements of the First to Third Groups When Present Together, with Special Regard to Spot Tests, Z. Anorg. Allgem. Chem. 140: 320 (1924).

104. Tedeschi, R. E., and F. W. Sunderman, Nickel Poisoning. V. The Metabolism of Nickel under Normal Conditions and After Exposure to Nickel Carbonyl, A.M.A. Arch. Ind. Health 16:486 (1957).

105. Thompson, R. J., G. B. Morgan, and L. J. Purdue, Analyses of Selected Elements in Atmospheric Particulate Matter by Atomic Absorption, Preprint. Presented at the Instrument Society of America Symposium, New Orleans, La. (May 5-7, 1969).

106. Threshold Limit Values for 1967, Adopted at the 29th Annual Meeting of the American Conference of Governmental Industrial Hygienists, Chicago, Ill. (May 1-2, 1967).

107. Tipton, I. H., and J. J. Shafer, Statistical Analysis of Lung Tract Element Levels, Arch. Environ. Health 8(1):58 (1964).

108. Tso, T. C., Micro- and Secondary-Elements in Tobacco, Botan. Bull. Acad. Sinica 7(1):28 (1966).

109. Wase, A. W., D. M. Goss, and M. J. Boyd, The Metabolism of Nickel. I. The Spatial and Temporal Distribution of Ni-63 in the Mouse, Arch. Biochem. 51:1 (1954).

110. Watt, T. L., and R. R. Vauman, Nickel Earlobe Dermatitis, Arch. Dermatol. 98:155 (1968).

111. Weber, C. W., and B. L. Reid, Nickel Toxicity in Growing Chicks, J. Nutr. 95:612 (1968).

112. West, P. W., et al., Transfer, Concentration, and Analysis of Collected Air-Borne Particulates Based on Ring Oven Techniques, Anal. Chem. 32(8):943-6 (1960).

113. Williams, W. J., The Pathology of the Lung of Five Nickel Workers, Brit. J. Ind. Med. 14:235 (1958).

APPENDIX

APPENDIX

TABLE 5

MORTALITY IN ONTARIO NICKEL REFINERY WORKERS BY EXPOSURE GROUPS 1930-1965[68]

Exposure Group	Sinus Cancer Deaths		Pulmonary Cancer Deaths	
	Observed	Expected	Observed	Expected
1. Furnace workers	5	0.023	8	1.88
2. Maintenance staff	0	0.029	4	1.89
3. Electrolytic workers	0	0.014	1	1.26
4. Storeroom workers	0	0.011	0	1.07
5. Office workers	0	0.006	2	0.41
6. Mixed exposure[a]	2	0.035	6	2.57
7. Mixed exposure[b]	8	0.026	15	2.15
8. Mixed exposure[c]	1	0.022	1	1.47
Total	16	0.166	37	12.711

[a]Workers with less than 3 years' exposure in groups 1 and 2, plus other work in the refinery.

[b]Workers with 3 years' or more exposure in group 1, plus other work in the refinery.

[c]Workers with 3 years' or more exposure in group 2, plus other work in the refinery.

APPENDIX

TABLE 6

ANALYSIS OF FLUE DUST FROM ONTARIO NICKEL REFINERY[40]

Substance	Percent
Cupric oxide (CuO)	3.4
Nickel sulfate ($NiSO_4 \cdot 6H_2O$)	20.0
Nickel sulfide (Ni_2S_3)	59.0
Nickel oxide (NiO)	6.3
Cobalt oxide (CoO)	1.0
Ferric oxide (Fe_2O_3)	4.8
Silicon dioxide (SiO_2)	1.2
Moisture	7.3
Other	2.0

APPENDIX

TABLE 7

NICKEL CONCENTRATION IN THE ORGANS OF MICE EXPOSED TO NICKEL CARBONYL[54]

Exposure Group	Concentration (µg/g of tissue)					
	Lung	Liver	Kidney	Heart	Brain	Intestine
1[a]	8.17	11.37	4.66		1.53	5.12
2[b]	7.98	7.47	3.89	2.01	1.22	4.86
3[c]	5.83	5.61	3.32	1.50	0.49	4.45

[a]Mice exposed to 5 ppm 10 times and 7.5 ppm 10 times.

[b]Mice exposed to 5 ppm 10 times and 7.5 ppm 5 times.

[c]Mice exposed to 5 ppm 5 times and 7.5 ppm 5 times.

APPENDIX

TABLE 8

DISTRIBUTION OF NICKEL-63 IN RATS[a88]
(Dose in Percent per Gram of Fresh Tissue)

Tissue	Hours After Dose		
	0.25	6	72
Kidney	2.49	0.59	0.11
Adrenal	.92	.15	.03
Ovary	.90	.11	nd[b]
Lung	.81	.14	.01
Heart	.64	.11	nd[b]
Eye	.56	.13	.01
Thymus	.55	.12	nd[b]
Pancreas	.54	.12	nd[b]
Spleen	.48	.11	.01
Liver	.40	.08	nd[b]
Skin	.38	.07	nd[b]
Gastrointestinal tract	.33	.11	nd[b]
Muscle	.29	.04	nd[b]
Teeth	.21	.04	.01
Femur	.15	.03	nd[b]
Brain	.15	.04	nd[b]
Adipose tissue	.14	.02	nd[b]
Carcass			nd[b]

[a]Rats injected with $Ni^{63}Cl_2$ in saline solution 0.74 or 1.47 µg/rat (2.5 or 5 µ curie/rat).

[b]nd = Not detectable.

APPENDIX

TABLE 9

PRODUCTION AND CONSUMPTION OF NICKEL[74]
(Short Tons)

	1957-61 (average)	1962	1963	1964	1965	1966
United States:						
Mine production	13,395	13,110	13,394	15,420	16,188	15,036
Plant production						
Primary	11,779	11,217	11,432	12,185	13,510	13,237
Secondary (from scrap)	9,801	11,108	18,996	23,114	19,407	26,777
Exports	30,024	27,641	60,927	68,502	20,935	26,364
Import for consumption	114,400	123,000	119,000	129,000	163,000	141,000
Consumption	108,163	118,677	124,478	146,920	172,084	187,833
Stocks Dec. 31: Consumer	16,483	13,450	17,191	17,185	14,047	31,375
Price (cents per pound)	74-81¼	81¼-79	79	79	79-77 3/4	77 3/4-85¼
World:						
Production	325,400	394,000	392,000	423,000	481,000	475,000

APPENDIX

TABLE 10

NICKEL (EXCLUSIVE OF SCRAP) CONSUMED IN THE UNITED STATES, BY USES[74]
(Short Tons)

Use	1957-61 (average)	1962	1963	1964	1965	1966
Alloy steels	16,461	18,608	19,727	24,679	27,009	27,807
Cast irons	4,699	5,503	5,901	6,605	6,937	7,286
Copper base alloys (including coinage)						9,937[a]
Electrical resistance alloys[b]	9,835	12,862	13,505	15,291	18,464	5,423
Electroplating:						
Anodes	15,455	16,953	18,621	19,446	19,450	13,828
Solutions	897	904	1,050	1,645	2,037	1,925
Nickel alloys	26,492	28,215	24,794	23,639	37,082	47,366[a]
Permanent magnets	823	910	777	664	828	807
Stainless and heat resisting steels	29,315	29,711	34,140	48,301	51,700	65,910
Other[c]	4,186	5,011	5,963	6,650	8,577	7,544
Total	108,163	118,677	124,478	146,920	172,084	187,833

[a]Copper base and nickel alloys formerly published together as nonferrous.

[b]Before 1966, included high temperature alloy, now shown under nickel alloys.

[c]Catalysts, ceramics, chemicals (other than for electroplating), iron-nickel alloys, metal powder products, welding rods, etc.

APPENDIX

TABLE 11

REFINERS OR PROCESSORS OF NICKEL
IN THE UNITED STATES IN 1963[73]

Refiner or Processor	Location of Plant	Nickel Products Made
Allied Chemical Corp. General Chemical Division	Marcus Hook, Pa.	Carbonate, salts
American Metal Climax, Inc.	Carteret, N.J.	Sulfate
American Smelting and Refining Co.	Perth Amboy, N.J.	Sulfate
Baker Chemical Co., J. T.	Phillipsburg, N.J.	Carbonate, salts
Hall Chemical Co.	Wickcliffe, Ohio	Carbonate
Hanna Nickel Smelting Co.	Riddle, Oreg.	Ferronickel
Harshaw Chemical Co.	Cleveland, Ohio	Carbonate, salts
International Nickel Co. of Canada, Ltd.	Huntington, W.Va.	Alloys, metal
McGean Chemical Co.	Cleveland, Ohio	Carbonate, salts
Nuodex Products Co., Inc.	Elizabeth, N.J.	Salts
Phelps Dodge Refining Corp.	Laurel Hill, N.Y.	Sulfate
Phelps Dodge Refining Corp.	El Paso, Tex.	Sulfate
Shepherd Chemical Co.	Cincinnati, Ohio	Carbonate, hydrate salts

APPENDIX

TABLE 12

NICKEL IN COAL ASH[1]

Source of Coal	Nickel in Ash (percent)
United States	
Northern Great Plains	0.0003-0.059
Texas, Colorado, North and South Dakota	0.01 -1.0
South Dakota	0.12
West Virginia	0.013 -0.079
Pennsylvania (anthracite)	0.01 -0.09
Australia	0.001 -0.06
Nova Scotia	0.0052-0.0645
Norway, Spitsbergen	0.001 -0.01
Germany, Newrode	0.11
Germany	0.3 max
England, Newcastle	0.079
England (vitrain)	0.05 -0.3
Russia	0.47 -1.02

TABLE 13

NICKEL EMISSIONS FROM COAL-FIRED POWER PLANTS[31]

Type of Boiler	µg/scf Before Fly Ash Collection	µg/scf After Fly-Ash Collection
Vertical[a]	1,100	250
Corner[a]	2,000	130
Front-wall[b]	2,900	170
Spreader-stoker[c]	830	350
Cyclone-fired unit[b]	2,400	510
Horizontally opposed[c]	4,600	690

[a]Fly-ash collector is cyclone-type separator followed by an electrostatic precipitator.

[b]Fly-ash collector is an electrostatic precipitator.

[c]Fly-ash collector is a cyclone-type separator.

TABLE 14

AVERAGE CONCENTRATIONS OF SUSPENDED PARTICULATES AND NICKEL AT 30 URBAN NASN STATIONS FOR THE PERIODS 1957-1960 AND 1961-1964[70]

Station	1957-1960 Susp. Part. ($\mu g/m^3$)	1957-1960 Ni ($\mu g/m^3$)	1957-1960 % Ni*	1961-1964 Susp. Part. ($\mu g/m^3$)	1961-1964 Ni ($\mu g/m^3$)	1961-1964 % Ni*
1 Atlanta, Ga.	125	.021	.017	104	.012	.012
2 Baltimore, Md.	141	.057	.040	145	.071	.049
3 Boise, Idaho	114	.037	.032	90	.006	.007
4 Boston, Mass.	156	.099	.063	144	.076	.053
5 Chattanooga, Tenn.	246	.024	.010	199	.018	.090
6 Charleston, W.Va.	217	.058	.027	271	.040	.015
7 Chicago, Ill.	190	.044	.023	170	.048	.028
8 Cincinnati, Ohio	145	.024	.017	131	.018	.014
9 Cleveland, Ohio	165	.035	.021	135	.027	.020
10 Columbus, Ohio	154	.045	.029	106	.024	.023
11 Denver, Colo.	139	.031	.022	146	.028	.019
12 Des Moines, Iowa	174	.016	.009	128	.010	.008
13 Detroit, Mich.	139	.037	.027	125	.020	.016
14 E. Chicago, Ind.	206	.202	.098	218	.123	.056
15 El Paso, Tex.	224	.015	.007	156	.015	.007
16 Indianapolis, Ind.	174	.023	.013	148	.036	.024
17 Los Angeles, Calif.	186	.055	.030	151	.041	.027
18 Milwaukee, Wisc.	155	.029	.019	146	.023	.016
19 New Orleans, La.	91	.025	.027	89	.022	.025
20 Newark, N.J.	113	.057	.050	113	.084	.074
21 Oklahoma City, Okla.	71	.013	.018	83	.014	.017
22 Omaha, Neb.	139	.018	.013	101	.013	.013
23 Philadelphia, Pa.	162	.082	.050	166	.075	.045
24 Phoenix, Ariz.	240	.038	.016	214	.019	.009
25 Pittsburgh, Pa.	166	.042	.025	179	.028	.016
26 St. Louis, Mo.	175	.018	.018	134	.013	.013
27 San Francisco, Calif.	81	.029	.036	68	.023	.034
28 Seattle, Wash.	125	.079	.063	68	.059	.087
29 Tacoma, Wash.	111	.051	.046	96	.038	.040
30 Washington, D.C.	111	.049	.044	98	.040	.041
Average	154.5	.045	.030	137.4	.035	.027

*% Ni = $\left(\frac{\text{Ni}}{\text{Susp. Part.}}\right)$ 100.

APPENDIX

TABLE 15

NICKEL IN THE ATMOSPHERE AT CINCINNATI AND INDIAN CREEK, 1967[64]

	Cincinnati[a]				Indian Creek[b]			
	max	min	avg	max/min ratio	max	min	avg	max/min ratio
Concentration, ($\mu g/m^3$)	0.06	<0.01	0.02	>6.0	0.03	<0.01	0.01	>3.0
Mass median diameter (μ)	>10	<0.1	1.1	>100	2.8	<0.48	0.85	>5.8

[a]Samples collected in downtown Cincinnati, May 24-June 3, 1967.

[b]Samples collected at the Indian Creek Wild Life Preserve, May 24-June 3, 1967.

TABLE 16

PHYSICAL PROPERTIES OF NICKEL AND NICKEL CARBONYL[71,73,80]

	Nickel	Nickel Carbonyl
Formula	Ni	$Ni(CO)_4$
Normal state	Solid	Liquid
Melting point	1,453°C	-25°C
Boiling point	2,839°C	43°C
Decomposition point		>60°C
Color	grayish-white	Colorless
Odor threshold		1-3 ppm
Density (relative to air)		5.9 (Air=1) @ 25°C
Density (g/cm^3)	8.902 @ 25°C	1.32 @ 25°C
Solubility in water	Insoluble	200 ppm
1,000 $\mu g/m^3$		0.143 ppm
1 ppm		6,700 $\mu g/m^3$
Vapor pressure (vp) of nickel carbonyl		temp (°C) / vp (mm)
		-23 / 40
		-15.9 / 60
		- 6 / 100
		8.8 / 200
		25.8 / 400
		43 / 760
		60 / decomposes

APPENDIX

TABLE 17

ANIMAL EXPOSURE TO NICKEL CARBONYL

Animal	Dose	Exposure	Effects	Ref.
Man	Unknown	Accidental exposure	Initial: transient malaise; 12-36 hr later: dyspnea, cyanosis, productive cough	21
			Initial: dizziness, headache, sensation of substernal constriction; 10 hr-8 days later: increase in respiratory frequency, decrease in tidal volume, cyanosis (dimercaprol beneficial)	93
Dog	2,000-2,500 µg/liter	30 min	4-5 days later: increase in respiratory frequency	97
Rat	800-1,000 µg/liter	30 min	4-5 days later: increase in respiratory frequency	
5 dogs	200-1,000 µg/liter	30 min	~99% of Ni excreted in urine within 6 days	104
1 cat	1,300 (500-1,950) µg/liter in absolute alcohol	30 min/day, 6 exposures (125 days)	Lungs: severe congestion and edema in those dying immediately; extensive pneumonitis in survivors of one or more days. Liver: nearly complete necrosis of pericentral cells. Spleen: focal necrosis, reticular degeneration, accumulated megakaryocytes. Kidneys: tubular epithelial degeneration and glomerular degeneration.	56
12 cats	190-2,430 µg/liter in absolute alcohol	30 min	LC_{50}, 1,900 µg/liter	
118 mice	15.5-90 µg/liter in absolute alcohol	30 min	LC_{50}, 67 µg/liter	
5 mice	76 (16-190) µg/liter	30 min/day 10 exposures (48 days)	2 died	
75 rats (Wistar)	170-500 µg/liter in absolute alcohol	30 min	LC_{50}, 240 µg/liter	
6 rats (Wistar)	380 (85-540) µg/liter in absolute alcohol	30 min/day 10 exposures (48 days)	1 died; ~50% increase in Hb	

(continued)

APPENDIX

TABLE 17 (Continued)

ANIMAL EXPOSURE TO NICKEL CARBONYL

Animal	Dose	Exposure	Effects	Ref.
285 rats	600,000 μg/m^3	30 min	214 died in 3 weeks; 16 developed malignant tumors	92
60 rats	600,000 μg/m^3 +50 μg/g dithiocarb	30 min	All survived 3 wk; 17 developed malignant tumors	
19 rats	control solvent	30 min	All survived 3 wk; 5 developed malignant tumors	
19 rats	control solvent +50 μg/liter dithiocarb	30 min	All survived 3 wk; 6 developed malignant tumors	
64 rats	30,000 μg/m^3	30 min 3 times/wk	All survived 3 wk; 7 developed malignant tumors	
32 rats	solvent control	30 min 3 times/wk	All survived 3 wk; 4 developed malignant tumors	
176 rats	30,000-250,000 μg/m^3	30 min 3 times/wk	4 rats died of pulmonary cancer after 24 months	96
137 rats (Wistar) 145-273g	30-60 μg/liter in 50% C_2H_5OH & $(C_2H_5)_2O$	30 min/day 3 days/wk (52 wk)	Decreased growth rate, high mortality rate; wt of heart, lungs, and adrenals significantly elevated; extensive pulmonary lesions; much squamous metaplasia or bronchial epithelium	95
64 rats	4 ppm	3 times/wk 24 months	1 Squamous cell carcinoma	92
	4 ppm	3 times/wk 26 months	1 Adenocarcinoma	
	35 ppm	Single exposure	1 Anaplastic carcinoma	
	80 ppm	Single exposure	1 Adenocarcinoma[a]	
	80 ppm	Single exposure	1 Anaplastic carcinoma[b]	

[a] 24 months after exposure.

[b] 26 months after exposure.

APPENDIX

TABLE 18

CONCENTRATION OF NICKEL IN THE AIR[2,4,5,6]
(In μg/m³)

Location	1954-59[a]		1960		1961		1962		1963		1964		1965	
	Max	Avg[b]	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg
Alabama														
Birmingham											.043	.016	.011	.004
Huntsville									.000	.000				
Alaska														
Anchorage	.120	.017												
Point Woronzof[c]	.200	.030												
Arizona														
Phoenix							.048	.025			.040	.013		
California														
Los Angeles					.150	.043	.130	.049	.091	.030				
Pasadena	.100	.030					.064	.047						
San Francisco	.030	.008					.120	.025	.083	.021				
San Jose	.040	.016											.019	.012
San Leandro	.090	.017												
Santa Barbara							.017	.014						
Colorado														
Denver	.020	.004					.160	.038	.097	.035	.066	.012		
Denver County[c]	.005	.002												
Pueblo									.008	.006				
Connecticut														
Norwich									.033	.027				
Waterbury	2.800	.113												
District of Columbia														
Washington	.040	.024					.100	.038	.160	.040	.110	.041		
Florida														
St. Petersburg							.009	.004						
Tampa	.020	.006							.032	.014				
Georgia														
Atlanta	.060	.010							.022	.012			.013	.007
Idaho														
Boise			.015	.009			.023	.006			.011	.005	.000	.000

(continued)

APPENDIX

TABLE 18 (Continued)

CONCENTRATION OF NICKEL IN THE AIR[2,4,5,6]
(In μg/m³)

Location	1954-59[a]		1960		1961		1962		1963		1964		1965	
	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg
Illinois														
Chicago	.100	.018			.160	.054			.190	.050	.088	.042		
Cicero							.110	.040						
East St. Louis	.200	.020							.066	.024				
Joliet									.023	.017				
North Chicago									.025	.009				
Springfield									.014	.013				
Indiana														
East Chicago	.100	.018									.690	.123		
Indianapolis					.073	.034	.150	.037			.053	.014		
Muncie									.012	.003				
Iowa														
Cedar Rapids									.015	.014				
Des Moines			.031	.014			.036	.013			.016	.007		
Kentucky														
Louisville	.086	.010												
Louisiana														
Lake Charles							.000	.000						
New Orleans	.007	.002					.140	.031	.036	.012				
Maryland														
Cumberland									.014	.013				
Baltimore	.084	.041			.230	.081	.170	.052			.270	.080	.045	.034
Massachusetts														
Boston	.300	.042									.170	.076		
Everett	.080	.026												
Middlesex County[c]	.030	.009												
Michigan														
Detroit							.048	.020	.070	.020	.120	.030		
Grand Rapids									.039	.033				
Minnesota														
Minneapolis	.060	.008									.013	.003		
St. Paul							.062	.020						

(continued)

APPENDIX

TABLE 18 (Continued)

CONCENTRATION OF NICKEL IN THE AIR[2,4,5,6]
(In μg/m³)

Location	1954-59[a]		1960		1961		1962		1963		1964		1965	
	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg
Mississippi														
Jackson County[c]													.013	.012
Missouri														
Kansas City	.030	.008												
Shannon County[c]													.0026	.0017
St. Louis	.050	.013					.037	.022	.038	.012	.096	.017		
Montana														
Helena											.011	.004		
Glacier National Park[c]													.0097	.0033
Nebraska														
Lincoln							.008	.005						
Omaha	.031	.018					.019	.011						
Thomas County[c]													.0017	.0011
Nevada														
Las Vegas							.025	.007	.020	.005	.036	.012		
Reno									.039	.031				
White Pine County[c]													.0020	.0008
New Hampshire														
Coos County[c]													.0031	.0021
New Jersey														
Bayonne									.110	.077			.062	
Bridgeton													.013	.011
Camden	.095	.025					.130	.080						
Elizabeth	.059	.019												
Jersey City	.150	.043												
Lakehurst[c]	.038	.008												
Newark							.320	.080			.340	.093		
Paterson									.097	.070				
Paulsboro	.051	.017												
Perth Amboy	.053	.019												
Trenton	.045	.016												

(continued)

APPENDIX

TABLE 18 (Continued)

CONCENTRATION OF NICKEL IN THE AIR[2,4,5,6]
(In μg/m³)

Location	1954-59[a]		1960		1961		1962		1963		1964		1965	
	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg
New Mexico														
Albuquerque													.000	.000
Rio Arriba County[c]													.0030	.0024
New York														
Buffalo							.053	.024						
Cape Vincent[c]													.0059	.0033
Glen Cove							.057	.039						
Massena					.021	.019								
Mount Vernon					.094	.068								
New York	.210	.065					.460	.159	.360	.153	.290	.109		
Rochester			.360	.052	.079	.049								
Troy							.053	.031						
New Rochelle					.100	.065								
North Carolina														
Asheville			.024	.014										
Cape Hatteras[c]													.0053	.0026
Charlotte											.027	.005		
Durham									.022	.017				
Winston-Salem							.034	.017						
Ohio														
Akron													.023	.017
Cincinnati	.099	.013	.049	.025			.038	.020	.037	.016	.044	.018		
Cleveland							.046	.016	.170	.035	.140	.031		
Columbus							.051	.022						
Youngstown	.053	.035					.049	.012	.029	.014				
Oklahoma														
Cherokee County[c]													.0019	.0013
Oklahoma City							.020	.008						
Tulsa					.007	.000								
Oregon														
Curry County[c]													.0028	.0017
Portland	.100	.065							.068	.031	.120	.048		

(continued)

APPENDIX

TABLE 18 (Continued)

CONCENTRATION OF NICKEL IN THE AIR[2,4,5,6]
(In μg/m³)

Location	1954-59[a]		1960		1961		1962		1963		1964		1965	
	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg
Pennsylvania														
Allentown					.080	.025							.018	
Altoona	.010	.006							.022	.017			.011	.005
Bethlehem													.033	.019
Chester	.098	.016												
Clarion County[c]													.0044	.0039
Bristol	.017	.007												
Erie	.020	.005												
Johnstown													.052	.016
Lancaster							.042	.026						
Philadelphia	.130	.026	.330	.097			.140	.079	.140	.073	.210	.079		
Pittsburgh	.100	.014					.090	.027	.110	.028	.082	.025		
Scranton					.073	.031								
Williamsport	.200	.016												
Puerto Rico														
Bayamon	.033	.021												
Rhode Island														
East Providence									.038	.035				
Washington County[c]													.013	.0083
South Carolina														
Richland County[c]													.0026	.0013
South Dakota														
Black Hills Forest													.0019	.0007
Tennessee														
Chattanooga	.030	.005									.028	.018		
Memphis											.021	.002		
Nashville											.013	.004		
Texas														
Bellaire	.010	.001												
El Paso							.018	.009			.026	.013		
Fort Worth	.010	.003												
Houston	.060	.003									.028	.006		
Matagorda County[c]													.0031	.0018
Tyler									.019	.016				
Odessa									.025	.019				

(continued)

APPENDIX

TABLE 18 (Continued)

CONCENTRATION OF NICKEL IN THE AIR[2,4,5,6]
(In μg/m³)

Location	1954-59[a]		1960		1961		1962		1963		1964		1965	
	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg
Utah														
Salt Lake City	.030	.011									.020	.004		
Vermont														
Orange County[c]													.0076	.0045
Virginia														
Portsmouth													.022	.019
Richmond													.029	.022
Shenandoah Park[c]													.0028	.0024
Washington														
Seattle	.180	.078					.260	.071	.220	.046				
Spokane					.023	.016								
Tacoma							.084	.033	.097	.041				
West Virginia														
Charleston	.100	.012									.077	.028		
Huntington			.210	.119										
Kanawha County[c]	.020	.003												
Wisconsin														
Door County[c]													.0021	.0017
Milwaukee	.070	.029									.075	.023		
Wyoming														
Cheyenne											.008			
Yellowstone Park[c]													.0000	.0000

[a]The data in this column may include only one year or the average of all measurements made during these years.

[b]Avg = arithmetic mean.

[c]All locations are urban unless marked [c], which indicates nonurban.

APPENDIX

TABLE 19. PROPERTIES, TOXICITY, AND USES OF NICKEL AND SOME NICKEL COMPOUNDS[71]

Compounds	Properties	Toxicity	Uses
Nickel Ni	Lustrous white, hard, ferromagnetic metal mp 1,453° bp 2,732° Soluble in dilute HNO_3 Density = 8.90	May cause dermatitis in sensitive individuals. Ingestion of soluble salts causes nausea, vomiting, diarrhea	In nickel-plating; for various alloys such as new silver, Chinese silver, German silver; for coins, electrotypes, storage batteries, magnets, lightning rod tips, electrical contacts and electrodes, spark plugs, machinery parts; as catalyst for hydrogenation of oils and other organic substances. Raney ickel: As catalyst for hydrogenation of organic compounds with gaseous hydrogen. Usually from 1 to 10% of the substance to be reduced is employed. Is active at room temperature and at 1 atm pressure, but is also used at high temperatures and high pressures. Probably the largest use of nickel is in the manufacture of Monel metal, stainless steels, and nickel-chrome resistance wire; in alloys for electronic and space applications
Nickel acetate $Ni(C_2H_3O_2)_2$- $4H_2O$	Green crystalline mass or powder bp 16.6°C Density 1.744		
Nickel arsenate $Ni_3(AsO_4)_2 \cdot$ $8H_2O$	Yellowish-green powder Density 4.982 Insoluble in water		

(continued)

APPENDIX

TABLE 19. PROPERTIES, TOXICITY, AND USES OF NICKEL AND SOME NICKEL COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Nickel bromide $NiBr_2 \cdot 3H_2O$	Yellowish-green very deliquescent crystals mp 963°C		
Nickel carbonate hydroxide $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$	Green, odorless powder		In nickel-plating, as catalyst for hardening of fats, in ceramic colors and glazes
Nickel carbonyl $Ni(CO)_4$	Yellow volatile liquid mp -25°C bp 43°C Decomposes at 60°C Insoluble in water Soluble in most organic solvents	Poisonous! Vapors may cause irritation, congestion, and edema of lungs. Prolonged exposure may cause cancer of lungs, nasal sinuses Odor threshold = 1-3 ppm	In refining nickel by the Mond process, as vapor-plating catalyst
Nickel chloride $NiCl_2 \cdot 6H_2O$	Green, deliquescent crystals or powder Sublimes at 973°C	LD iv in dogs 10,000 to 20,000 µg/kg	For nickel-plating cast zinc, manufacture of ink. The anhydrous salt as absorbent for NH_3 in gas masks
Nickel citrate $Ni_3(C_6H_5O_7)_2 \cdot 14H_2O$	Light green deliquescent powder Soluble in water		
Nickel cyanide $Ni(CN)_2 \cdot 4H_2O$	Apple green powder Insoluble in water	Poisonous!	In nickel-plating
Nickel dimethylglyoxime $C_8H_{14}N_4NiO_4$	Scarlet-red crystalline powder Sublimes at 250°C		As sunfast pigment in paints, lacquers, cellulose compounds, and cosmetics

(continued)

APPENDIX

TABLE 19. PROPERTIES, TOXICITY, AND USES OF NICKEL AND SOME NICKEL COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Nickel fluoride NiF_2	Yellow to green tetragonal crystals Sublimes in HF stream above 1,000°	Chronic exposure may cause mottling of teeth, changes in bones See nickel	
Nickel formate $Ni(HCOO)_2$	Fine green monoclinic crystals		In manufacture of nickel, preparation of nickel catalysts for organic reactions (particularly hydrogenation catalysts)
Nickel hydroxide $Ni(OH)_2-H_2O$	Apple-green powder, ignited in air at about 400° Insoluble in water		
Nickel iodide $NiI_2.6H_2O$	Bluish-green, very deliquescent crystals mp 797°		
Nickel monoxide NiO	Green powder Insoluble in water mp 1,990°		For painting on porcelain
Nickel nitrate $Ni(NO_3)_2.6H_2O$	Green, deliquescent crystals mp 56.7° bp 137°		In nickel-plating, manufacture of brown ceramic colors
Nickel oxalate $NiC_2O_4.2H_2O$	Light green powder Insoluble in water		
Nickel phosphate $Ni_3(PO_4)_2 7H_2O$	Light green powder Insoluble in water		On ignition yields "nickel-yellow"—a pigment used in oil and water colors

(continued)

APPENDIX

TABLE 19. PROPERTIES, TOXICITY, AND USES OF NICKEL AND SOME NICKEL COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Nickel potassium sulfate $K_2Ni(SO_4)_2 6H_2O$	Bluish-green crystals Soluble in water		
Nickel selenate $NiSeO_4.6H_2O$	Tetragonal crystals		
Nickel selenide NiSe	Silver-white cubic crystals, brittle		
Nickel selenite $NiSeO_3$	Yellow crystals		
Nickel sesquioxide Ni_2O_3	Gray-black powder Decomposes ~600°C		
Nickel sulfate $NiSO_4.6H_2O$	Emerald-green transparent crystals, sweet astringent taste	L.D.s.c. in guinea pigs 62 µg/g	In nickel-plating, as mordant in dyeing and printing fabrics, for blackening zinc and brass
Dicyclopentadienyl-nickel $(C_5H_5)_2Ni$	Sublimes at 130°C Soluble in alcohol		
bis (Cyclopentadienyl-nickel carbonyl) $(C_5H_5NiCO)_2$	mp 136°C		
Dicyclopentadiene-nickel $(C_5H_6)_2Ni$	mp 41-42°C		